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THE HYDRORETORTING ASSAY - A NEW TECHNIQUE FOR OIL SHALE ASSESSMENT

By

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INTRODUCTION

The Modified Fischer Assay technique developed by the U. S. Bureau of Mines for evaluation of oil yields from oil shale evolved from tests originally designed to measure the potential liquid yield obtained in coal pyrolysis operations. During the early decades of this century, procedures and operating conditions for the Fischer Assay were gradually modified to bring the results into line with oil yields obtained by typical thermal retorting processes of the day. The resulting test is now an ASTM standard method (Designation, D3904-80). While modern thermal retorting processes - when applied to Western U. S. (Eocene Age) oil shales - may produce oil yields which differ slightly from the results of this Fischer Assay Test, their yields are sufficiently close for Fischer Assay results to be accepted as a standard for assessment of the size of oil shale resources.

With the development of the HYTORT Process, it became necessary to develop an assay technique capable of measuring the substantially greater oil yields obtained by hydroretorting. In the future, we believe that evaluation of the magnitude of many oil shale resources will require utilization of the Hydroretorting Assay test described in this paper, as well as the conventional Modified Fischer Assay technique. In some instances, these techniques produce results which differ by factors of four or even greater. Acceptance and use of the Hydroretorting Assay technique described in this paper will, therefore, become a prerequisite for complete understanding of a given oil shale resource.

SPECIFICATIONS FOR THE HYDRORETORTING ASSAY PROCEDURE

From the beginning of the Hydroretorting Assay development project, it was recognized that direct measurement of actual yields of oil and water produced by hydroretorting oil shale samples was required. Although indirect techniques were briefly considered, the need for repeated empirical calibration of such techniques while moving from one oil shale deposit to another constituted a significant drawback which eventually caused rejection of these approaches. The problem thus became development of a laboratory procedure for reaction of small samples of oil shale with hydrogen and the design and construction of prototype test equipment to carry out that procedure. After the problem had been so defined, the following criteria were established for the design of the hydroretorting assay unit.

- The procedure should be simple enough to be conducted by a technician.
- The device used should be capable of field operation.
- Reproducibility of results should be aided by means of computer control of the device.
- In the prototype version, provision should be made for adjusting process conditions such as pressure, temperature, gas flow and heatup rate, to enable the operating conditions to be varied.
- A 100-gram sample should be used, for consistency with the Modified Fischer Assay test procedure.
- The device should be capable of duplicating the results of the Modified Fischer Assay.

The Hydroretorting Assay unit depicted in Figure 1 meets these criteria.

DESCRIPTION OF THE PROTOTYPE HYDRORETORTING ASSAY UNIT

The Hydroretorting Assay unit is capable of operating from atmospheric pressure up to 1000 psig, at temperature up to 1200°F and with heatup rate as high as 25°F/min. The unit consists of a 7/8-inch diameter, 16-inch long reactor tube mounted concentrically within a pressureretaining shell, 1-1/2-inches in diameter and 31 inches in length. This unit is enclosed in a three-zone electrically heated furnace. A schematic diagram of the unit is shown in Figure 2. The heaters are computer-controlled to achieve the desired heatup rate, to maintain the reactor at the operating temperature for a predetermined period of time and to maintain isothermal conditions vertically in the shale sample. Reactor temperatures are measured by a multipoint thermocouple inserted in the shale bed. The metered feed gas (hydrogen or nitrogen) enters the bottom of the pressure shell, is preheated as it flows upward in the annular space surrounding the reactor tube and then enters the reactor and is cooled by an electric chiller. The condensibles are collected in a graduated glass container and the gaseous product is continuously depressurized and metered by a dry test meter prior to venting. Gas samples may be taken throughout the test if desired. Test data--temperatures, feed and product gas flow rates, and pressure--are continuously recorded.

Before conducting Hydroretorting Assay tests, representative shale samples are crushed to -8 mesh particle size and riffled into approximately 100-gram samples. The weight of the test sample is then recorded and the sample is charged into the reactor. The system is pressure-tested and purged with feed gas. The operating conditions are programmed into the microprocessor and a test is started by keying in the run command. The system is brought to the desired operating pressure and the gas flowrate is set. The furnace heaters are activated and adjusted to achieve the desired heatup rate. The reactor is maintained at the desired operating temperature for a predetermined period of time. At the end of the test, the furnace is shut down and the reactor is allowed to cool to about 200°F. The residual shale is removed and weighed; the liquid products collected in the graduated glass container are centrifuged; the water and oil volumes are measured; and the entire liquid sample is weighed. The unit is then ready for the next test. A typical output data sheet is shown in Figure 3. Tests take about four hours to complete.

A standardized set of assay conditions were established after a test program was conducted to survey results at various operating conditions and to compare them with larger scale HYTORT Process test results. These conditions are shown in Table I.

TABLE I

OPERATING CONDITIONS FOR THE STANDARD HYDRORETORTING ASSAY AND FOR FISCHER ASSAY SIMULATION

	Hydroretorting Assay	Fischer Assay Simulated
Sample, wt, gm	100	100
Particle size	-8 Mesh	-8 Mesh
Pressure, psig	1000	0
Heat-up rate, °F/min	25	22
Maximum temperature, °F	1000	932
Time at maximum temperature, min	30	40
Gal flow rate, SCF/hr	4 (H_2)	0.1 (N_2)

A standardization test series conducted on Indiana New Albany oil shale showed that Hydroretorting Assay tests on riffled splits of the same sample having a mean hydroretorting oil yield of 28.25 gal/ton exhibited a standard deviation of 1.23 gal/ton, or about 4%.

The Hydroretorting Assay test unit can also be operated with inert sweep gases at atmospheric pressure to provide an indication of oil yields in conventional, thermal retorting in a manner analogous to the Modified Fischer Assay.

Simulation of a conventional Modified Fischer Assay in this device requires a small flow of nitrogen because the Hydroretorting Assay unit reactor is shaped rather differently than a conventional Modified Fischer Assay retort. Tests were conducted on oil shale of the Western United States to determine the quality of simulation of Fischer Assay obtainable in the Hydroretorting Assay device. These test indicated that results within 2% of oil yields obtained by conventional Fischer Assay can be obtained in the Hydroretorting Assay under simulated Fischer Assay conditions. Agreement is excellent despite the use of nitrogen purge and the unit is capable of assessing oil shale response to conventional retorting as well as to hydroretorting.

Although the standardized hydroretorting test conditions which we have developed call for operation at 1000 psi, the Hydroretorting Assay unit can also be operated at other pressures. Temperature and heatup rate can also be varied. Therefore, the Hydroretorting Assay unit can serve as a first experimental step in determination of the economically-optimum conditions of operation for a given oil shale resource. Further, samples of product gas from the hydroretorting assay unit can be analyzed off-line using a mass spectrometer or a gas chromatograph. Coupled with ultimate analysis of raw and spent shale, this technique can be used to obtain the equivalent of a material

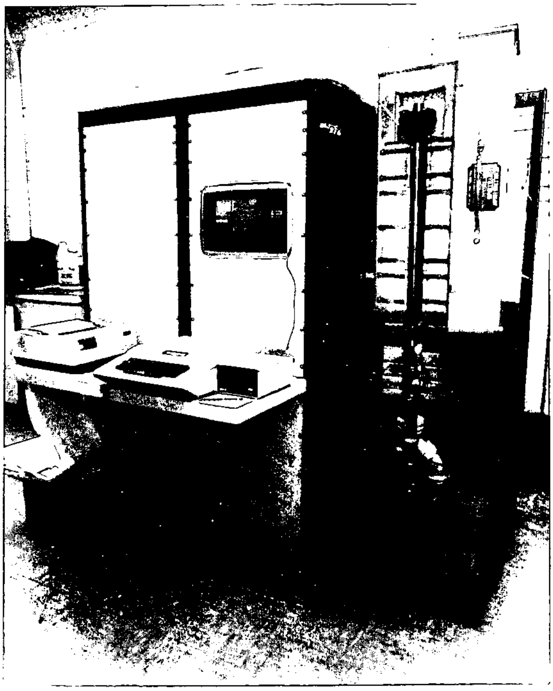

Figure 1. Hydroretorting Assay Unit

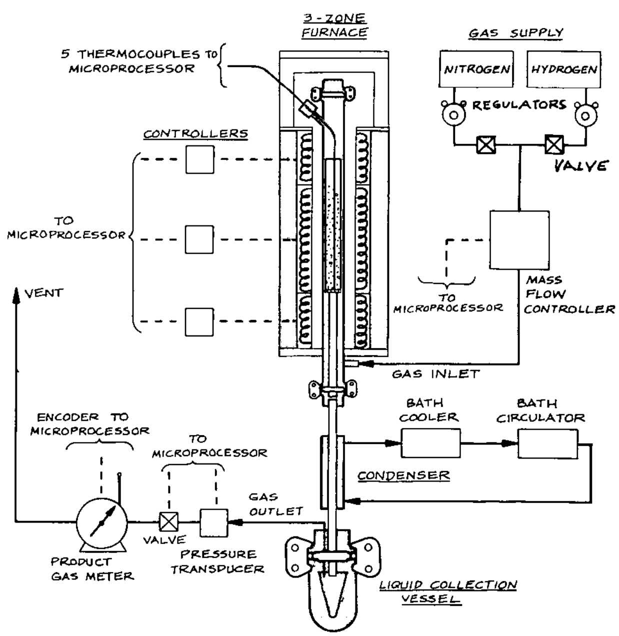

Figure 2
HYDRORETORTING ASSAY UNIT
SIMPLIFIED PROCESS FLOW DIAGRAM

COMPUTERIZED HYDRORETORTING ANALYSIS

RUN NUMBER	———
SAMPLE DESIGNATION	———
WEIGHT OF SAMPLE: GRAMS	100.06
GAS FLOW: SCFH	4.01
UNIT PRESSURE: PSIG	1000.4
RAMP: DEG./MIN.	24.26
MAXIMUM TEMPERATURE: °F	1005.8
TIME AT TEMPERATURE: MIN.	30
SOLIDS RESIDUE: GRAMS	74.53
TOTAL LIQUID PRODUCTS: CC.	19.8
VOLUME OF WATER: CC.	6.3
OIL PRODUCTION: GALS./TON	32.33

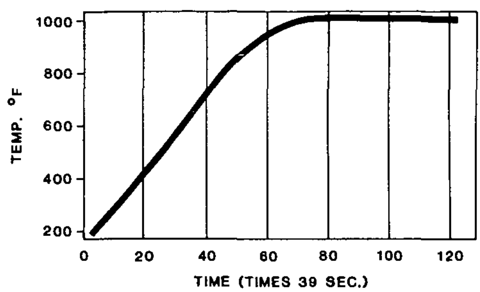

Figure 3. HYDRORETORTING ASSAY PRINTOUT

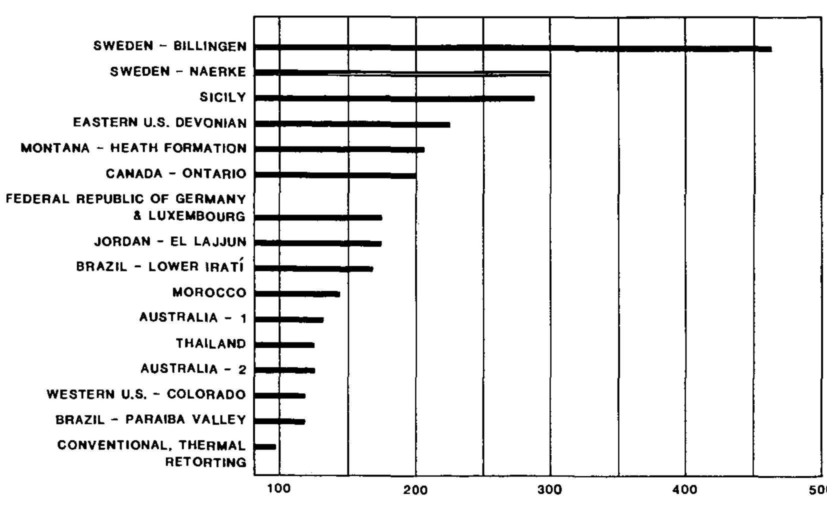

Figure 4. HYDRORETORTING ASSAY RESULTS FOR WORLD OIL SHALE SAMPLES

balance Fischer Assay for hydroretorting. Thus, the hydroretorting Fischer Assay unit has flexibility beyond that required for a device to merely measure oil yields.

HYDRORETORTING ASSAY TEST RESULTS

In co-operation with the U. S. Geological Survey and with various foreign survey personnel, HYCRUDE Corporation has conducted Hydroretorting Assay tests on samples from a number of the world's major oil shale resource areas. Selected test results are shown in Figure 4. These results indicate that the HYTORT Process can produce oil yields of over 400% of those obtained by conventional, thermal retorting in at least one instance, with a number of samples showing oil yields of more than 150% of Fischer Assay (Table II). In some instances, these results mean that oil yields over 30 gallons per ton can be produced from oil shale resources which would normally be considered too lean for commercial exploitation by conventional retorting processes.

TABLE II

SELECTED HYDRORETORTING ASSAY TEST RESULTS

Oil Shale Sample	Oil Yields: Fischer Assay gal/ton	Oil Yields: Hydroretorting Assay gal/ton
Sweden - Billingen	3.8	17.5
Sweden - Naerke	10.9	32.3
Sicily	4.4	12.2
Indiana - New Albany	12.5	28.2
Montana - Heath Formation	16.2	33.6
Canada - Ontario	10.0	21.1
Jordan - El Lajjun (Sample 1)	20.3	33.8
Jordan - El Lajjun (Sample 2)	32.8	57.0